

# Effects of a Silane Coupling Agent on the Exfoliation of Organoclay Layers in Polyurethane/Organoclay Nanocomposite Foams?

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**ABSTRACT:** An attempt was made to synthesize polyurethane (PU)/organoclay nanocomposite foams with high thermal insulation properties. The organoclay was modified by polymeric 4,4'-diphenylmethane diisocyanate (PMDI) with a silane coupling agent. The structure of the organoclay-modified PMDI with the silane coupling agent was determined by Fourier transform infrared spectroscopy and nuclear magnetic resonance. Transmission electron micrographs and wide-angle X-ray diffraction patterns showed that the interlayer distance increased for the PU/organoclay nanocomposites with the addition of the silane coupling agent. It was expected that the distance between the organoclay layers would increase and that the organoclay would be dispersed on a nanoscale in the PU matrix because of the organic/inorganic hybrid bond formation between the organoclay and silane coupling agent.

Compressive and flexural strengths of the PU/silane coupling agent/organoclay nanocomposite foams were similar to those of the PU/organoclay nanocomposite foams. However, the thermal conductivity appreciably decreased from 0.0250 to 0.0230 W/m h °C in the PU/silane coupling agent/organoclay nanocomposite foams. Scanning electron micrographs showed that the cell size of the PU/silane coupling agent/clay nanocomposite foams also decreased. On the basis of these results, it is suggested that the smaller cell size and lower thermal conductivity of the PU/silane coupling agent/organoclay nanocomposite foams were mainly due to enhanced exfoliation of the organoclay layers by the silane coupling reaction. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 376–386, 2008

**Key words:** organoclay; polyurethanes; nanocomposites

## INTRODUCTION

Polyurethane foam (PUF) is a unique polymer material having a wide range of physical and chemical properties.<sup>1–3</sup> Major applications of PUF are thermal insulation materials, structural materials, and automotive parts.<sup>4–16</sup> Many efforts have been made to improve the mechanical properties of PUF without lowering its thermal insulation properties.<sup>1–7</sup> Organoclay is one of the materials that can improve the mechanical strength of PUF because it has a high aspect ratio (as high as 100–1000), and the length and thickness of the clay are 0.1–10 μm and 1–3 nm, respectively.<sup>1–7</sup> Therefore, organically modified layered silicate (organoclay) as a special filler has been used in polymer/filler nanocomposites,<sup>1–28</sup> and the

physical properties of polymer/organoclay nanocomposites have turned out to be strongly dependent on the degree of dispersion of the particles.

To improve the dispersion of organoclay within the polyurethane (PU) matrix, researchers have tried to enhance the interaction between the polymer and organoclay of layered silicate components with various techniques such as ultrasonication,<sup>1,2</sup> the use of mixing conditions,<sup>4,5</sup> solution mixing,<sup>6</sup> *in situ* polymerization,<sup>7–11,17</sup> the use of intercalation agents,<sup>19–22</sup> and melt mixing.<sup>24</sup> Investigations have been conducted to determine the feasibility of using organic-inorganic hybrid materials by a coupling reaction. Macosko et al.<sup>9</sup> reported the exfoliation of silicate layers of organoclay in a PU matrix by the addition of hydroxyl and organotin functional groups to the clay surface. Chen et al.<sup>19</sup> reported that PU and silica hybrid films could be prepared by a sol-gel reaction via *in situ* polymerization or blending methods. The sol-gel process allows the synthesis of composites of PU films and elastomers with a silane coupling agent with molecular-level homogeneity.<sup>20,21</sup> However, most works have focused on PU films and elastomers and not on PUFs with microcellular structures.

It has been reported that the smaller cell size of PUF leads to lower thermal conductivity of PUF,

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and the cell size of PUF can be controlled by surfactants, catalysts, and the addition of clay particles.<sup>29–32</sup> Recently, research has turned toward the synthesis of PUF/organoclay nanocomposites with an intercalated organoclay structure in the polymer matrix in which small cells are evenly distributed.<sup>1,2</sup> In our earlier studies, it was found that the application of ultrasonic cavitation can produce a uniform dispersion of organoclay particles in the polymer matrix during the physical synthesis of PUF.

In this research, an attempt was made to obtain a uniform dispersion of organoclays by chemical bond formation between functional groups on the organoclay surface and the silane coupling agent. The silane coupling agent was expected to act as a bridge between the organoclay surface and polymer chain. The silane coupling agent was also expected to be effective in breaking up the organoclay agglomerates to obtain a small cell size in PUF/organoclay nanocomposites. Ultrasound was also applied during the coupling reaction to achieve a synergy effect for the both physical and chemical dispersions.

## EXPERIMENTAL

### Materials

The materials used in this study were obtained from commercial sources. Polymeric 4,4'-diphenylmethane diisocyanate (PMDI) was supplied by BASF Korea, Ltd. (Seoul, Korea). The average functionality of PMDI was 2.7, and the NCO content was 31.5 wt %. The equivalent weight and viscosity of PMDI were 135.0 g/mol and 550 cps, respectively. Pentaerythritol-based polyether polyol (OH value = 470), supplied by KPC Co. (Ulsan, Korea), was used for the preparation of the nanocomposites. The organoclay [30B clay with the organic modifier  $N^+(\text{CH}_2\text{CH}_2\text{OH})_2\text{CH}_3\text{T}$ , where T is tallow and C18/C16/C14 = 65/30/5] was supplied by Southern Clay Co. (Gonzales, TX). Dimethylcyclohexylamine, which was supplied from Air Products and Chemicals, Inc. (Hamilton, PA), was used as a catalyst. Poly(siloxane ether), used as a surfactant, was supplied by Osi Specialties, Inc. (Sistersville, WV). The polyol and organoclay were dehydrated before experiments at 90°C for 24 h in a vacuum oven. Other chemicals were used as received. *N*-β-(Aminoethyl)-γ-aminoethyltrimethoxysilane, which was used as a coupling agent, was supplied by Dami Polychem (Iksan, Korea).

### Sample preparation of the PMDI/silane coupling agent/organoclay mixture

The moisture of the organoclay was removed in a vacuum drying oven at 80°C for 24 h. PMDI and the silane coupling agent were premixed with a mechanical stirrer at 500 rpm in an oil bath at 60°C. The

mixture and organoclay were stirred at 500 rpm in an oil bath for 10 min. The contents of the coupling agent and organoclay were fixed at 0.1 and 3.0 wt % with respect to PMDI, respectively. After premixing, ultrasound (40 kHz, bolt clamped langevin type (BLT) vibrator type) was applied to the mixture of the organoclay and PMDI at 60°C for 2 h.<sup>1</sup> With our ultrasound equipment, a particular cooling system was not used because an appreciable temperature difference was not observed. Also, the PMDI/silane coupling agent/organoclay mixture was synthesized without ultrasound. PMDI/organoclay mixtures with and without the coupling agent were also prepared, and the properties of both mixtures were compared.

### Sample preparation of the PU/silane coupling agent/organoclay nanocomposite foams

PU/silane coupling agent/organoclay nanocomposites were prepared by the reaction between the polyol and PMDI, which was modified with the silane coupling agent and organoclay. The PU/silane coupling agent/organoclay nanocomposite foams were synthesized through a blowing reaction with a blowing agent such as distilled water or HFC-365mfc [hydrofluorocarbon ( $\text{CF}_3\text{CH}_2\text{CH}_2\text{CHF}_2$ )]. Polyether polyol, an amine catalyst, a surfactant, distilled water, and HFC-365mfc were used in the preparation of the nanocomposites, and the amount of each material was fixed at 100.0, 1.0, 1.5, 0.6, and 12.0 by weight, respectively. The polyol and PMDI/organoclay mixtures were put into the reactor and mixed for 30 s with a brushless-type stirrer. The stirrer speed was set at 3000 rpm throughout the mixing. After mixing, the reactants were poured into an open mold ( $250 \times 250 \times 100 \text{ mm}^3$ ) to produce free-rise foams, which were cured for 1 week at room temperature. Three replications for all foams were executed. The composition of the PU/silane coupling agent/organoclay nanocomposite foams is summarized in Table I. In our previous work, a detailed scheme of the PU synthesis was reported.<sup>1,2</sup>

### Fourier transform infrared (FTIR) spectroscopy

Infrared spectra of the samples were obtained with a PerkinElmer FTIR spectroscope (Buckinghamshire, UK) over the frequency range of 750–4000  $\text{cm}^{-1}$ . For each spectrum, 16 runs were collected and averaged. The FTIR specimen of the organoclay was prepared by the addition of approximately 1% sample powder to dry KBr powder and pressed onto a disc. The PMDI/organoclay nanocomposite samples were tested through the casting of a thin film from an *N,N*-dimethylformamide (DMF) solution onto a KBr window. The unreacted PMDI in the PMDI/silane

**TABLE I**  
**Compositions of the Materials Used in the Preparation of PU/Silane Coupling Agent/Organoclay Nanocomposite Foams**

Chemical	Weight ( $10^{-3}$ mol)	Weight (g)
PMDI	604.900	151.40
Organoclay	—	4.50
Silane coupling agent	0.6745	0.15
Polyol	714.290	100.00
Surfactant	0.493	1.50
Blowing agent (distilled water)	33.000	0.60
Blowing agent (HFC-365mfc)	81.081	12.00
Catalyst	9.992	1.00

coupling agent/organoclay mixture was washed off before the spectroscopic characterization. Unreacted  $-\text{Si}-\text{O}-\text{CH}_3$  (silane coupling agent) was also removed from the PMDI/silane coupling agent/organoclay mixture through washing with toluene. The prepared PMDI/silane coupling agent/organoclay mixture and acetone solution were centrifuged to remove unreacted  $-\text{Si}-\text{OH}$  (organoclay).

#### Nuclear magnetic resonance

The proton nuclear magnetic resonance ( $^1\text{H-NMR}$ ) spectra were recorded on a Varian (Palo Alto, CA) NMR-AS500 spectrometer at room temperature. Spectra were recorded for samples dissolved in deuterated tetrahydrofuran ( $\text{C}_4\text{D}_8\text{O}$ ). Chemical shifts were measured for the PMDI/silane coupling agent/organoclay mixture from the internal silane coupling agent and organoclay layers.

#### Thermogravimetric analysis (TGA)

The thermal stability of the PMDI/silane coupling agent and PMDI/silane coupling agent/organoclay mixture were observed with a thermogravimetric analyzer (TGA 2950, Du Pont Instruments, New Castle, DE) at a heating rate of  $10^\circ\text{C}/\text{min}$  from 50 to  $600^\circ\text{C}/\text{min}$  under a nitrogen atmosphere.

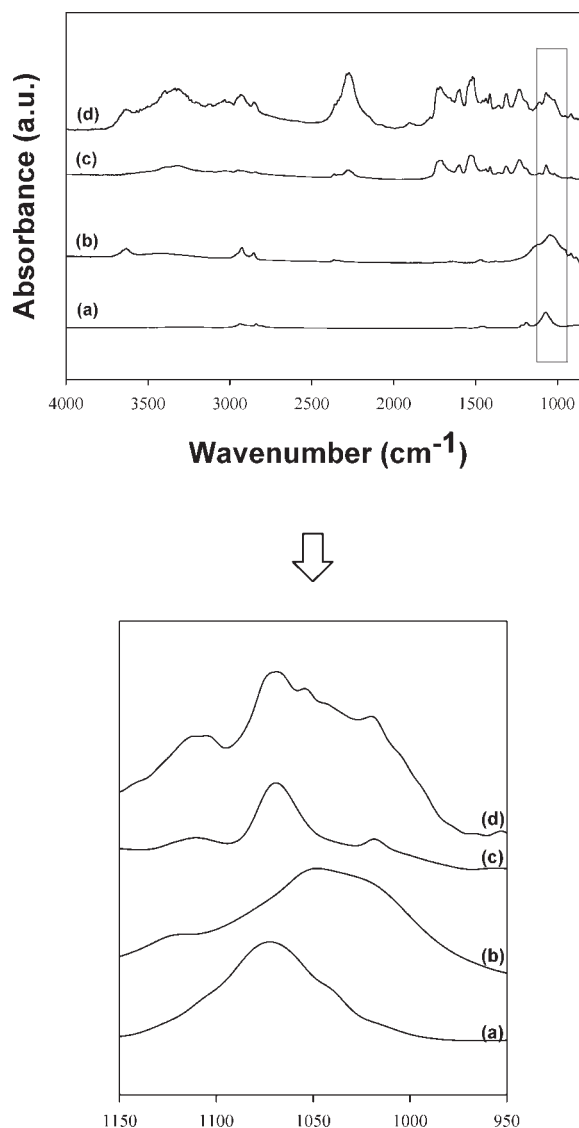
#### Scanning electron microscopy (SEM)

The morphology of the PU/silane coupling agent/organoclay nanocomposite foams was studied with an S-4300SE field emission scanning electron microscope (Hitachi, Tokyo, Japan). The samples were cryogenically fractured and coated with white gold before scanning. The accelerating voltage was 25 kV. The S-4300SE was used to observe the size of the cells on the PU/silane coupling agent/organoclay nanocomposite foam samples, which was measured with an Image-Pro Plus image analyzer (Media Cy-

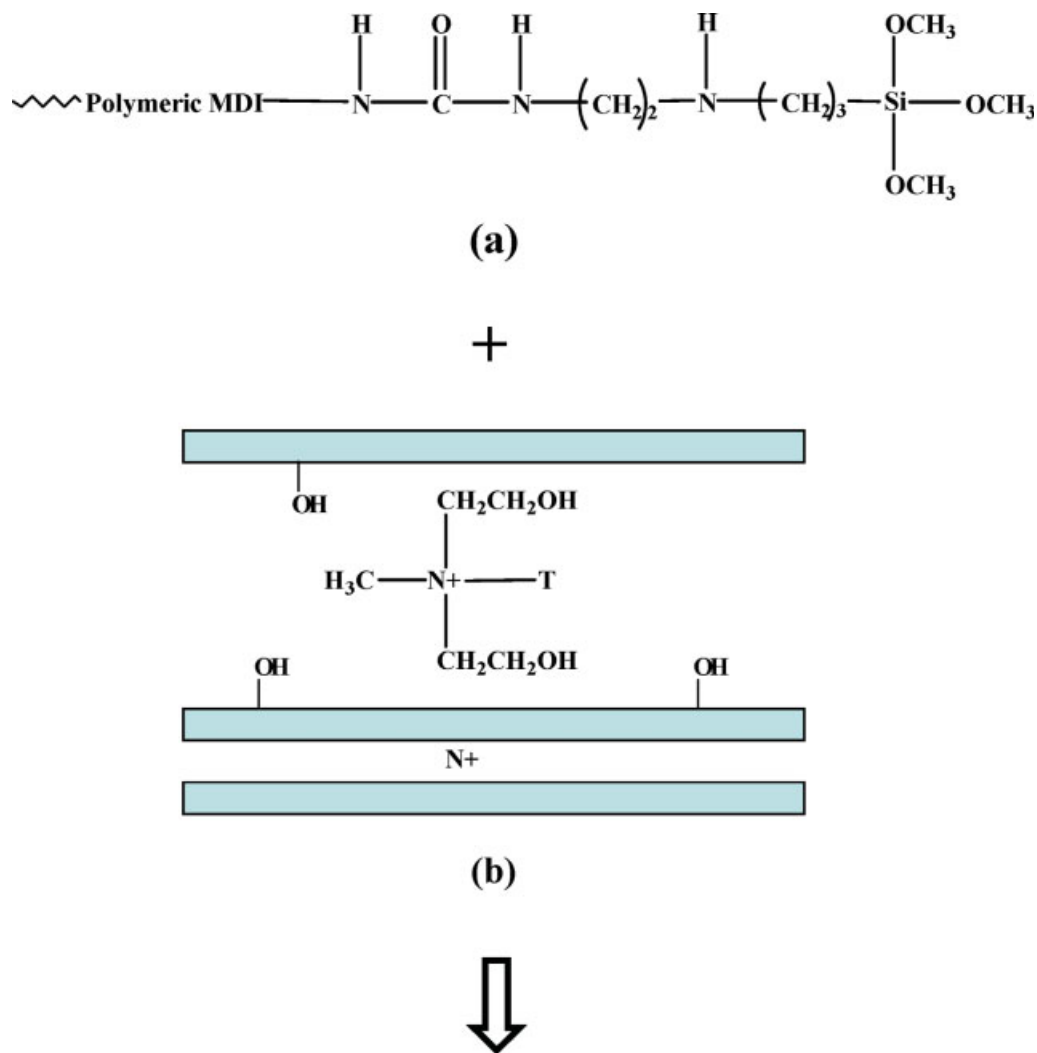
bernetics, Silver Spring, MD) and averaged, except for the largest and smallest cells.

#### Transmission electron microscopy (TEM)

TEM (Hillsboro, OR) micrographs were obtained with an FEI Tecnai  $G^2$  transmission electron microscope. The specimens were prepared by epoxy-embedding methods and microtomed at the ambient temperature. TEM was used to characterize the organoclay layer morphology in the PU/silane coupling agent/organoclay nanocomposites.



**Figure 1** FTIR spectra of (a) the silane coupling agent, (b) the organoclay, (c) the PMDI/silane coupling agent mixture, and (d) the PMDI/silane coupling agent/organoclay mixture.



**Figure 2** Schematic diagrams for the exfoliation process of organoclay layers for the PMDI/silane coupling agent/organoclay mixture: (a) the PMDI/silane coupling agent mixture, (b) the organoclay, (c) the organoclay and PMDI/silane coupling agent mixture, and (d) the exfoliation of organoclay layers with the PMDI/silane coupling agent/organoclay mixture. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Wide-angle X-ray diffraction (WAXD)

The distribution of clay layers in the PU/silane coupling agent/organoclay nanocomposites was measured with an X-ray diffractometer (model MXP-18, Mac Science, Tokyo, Japan). Cu K $\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) was used as an X-ray source at a generating voltage of 40 kV and a current of 30 mA. WAXD scans were obtained in the reflection mode with an incident X-ray wavelength of  $1.54 \text{ \AA}$  at a scan rate of  $1.0^\circ/\text{min}$ . The  $d$ -spacing was calculated by Bragg's law,  $d = n\lambda/2 \sin \theta$ , from the position of the (001) plane peak in the WAXD pattern.

### Thermal conductivity measurements

The thermal conductivity of the PU/silane coupling agent/organoclay nanocomposite foams was meas-

ured with a Holometrix Micromet model Lambda 2000 (Boston, MA) according to ASTM C 518. A sample was placed in the test section between the two plates, which were maintained at different temperatures during the test. Upon the achievement of thermal equilibrium and the establishment of a uniform temperature gradient throughout the sample, the thermal conductivity of the PU/silane coupling agent/organoclay nanocomposite foam samples was determined. The size of the specimen was  $300 \times 300 \times 50 \text{ mm}^3$  (width  $\times$  length  $\times$  thickness). The thermal conductivities of three specimens per sample were measured and averaged.

### Mechanical properties

The mechanical properties of the PU/organoclay foam and PU/silane coupling agent/organoclay

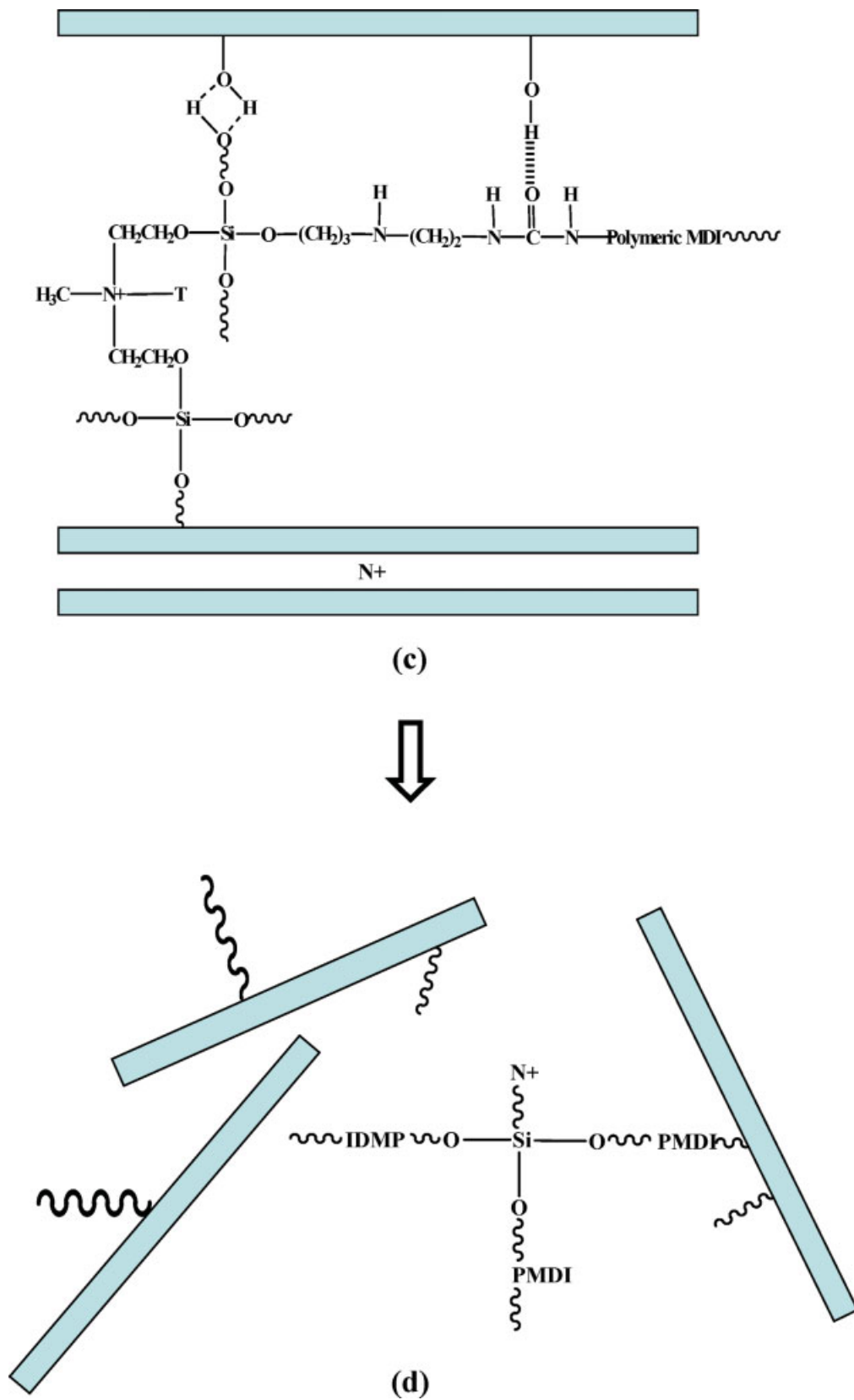


Figure 2 (Continued from the previous page)



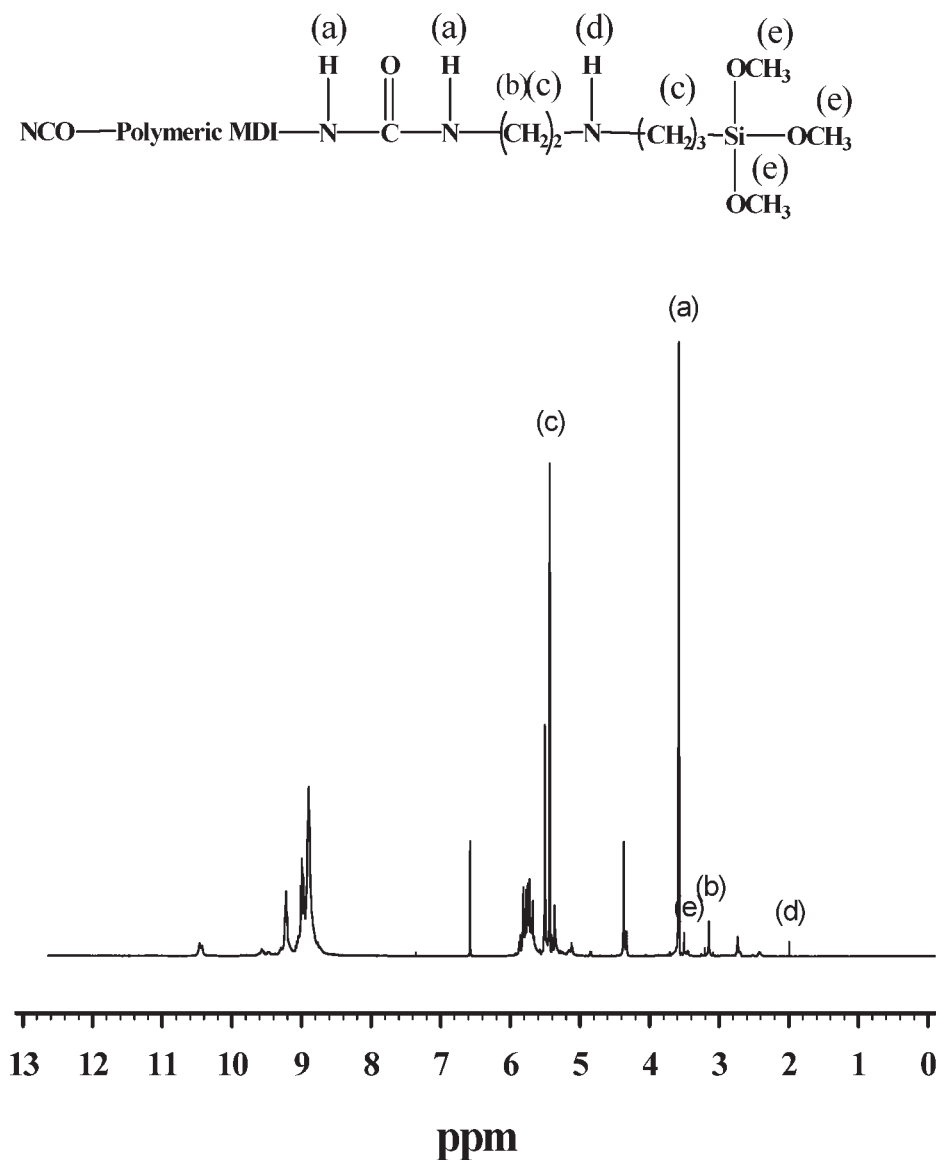


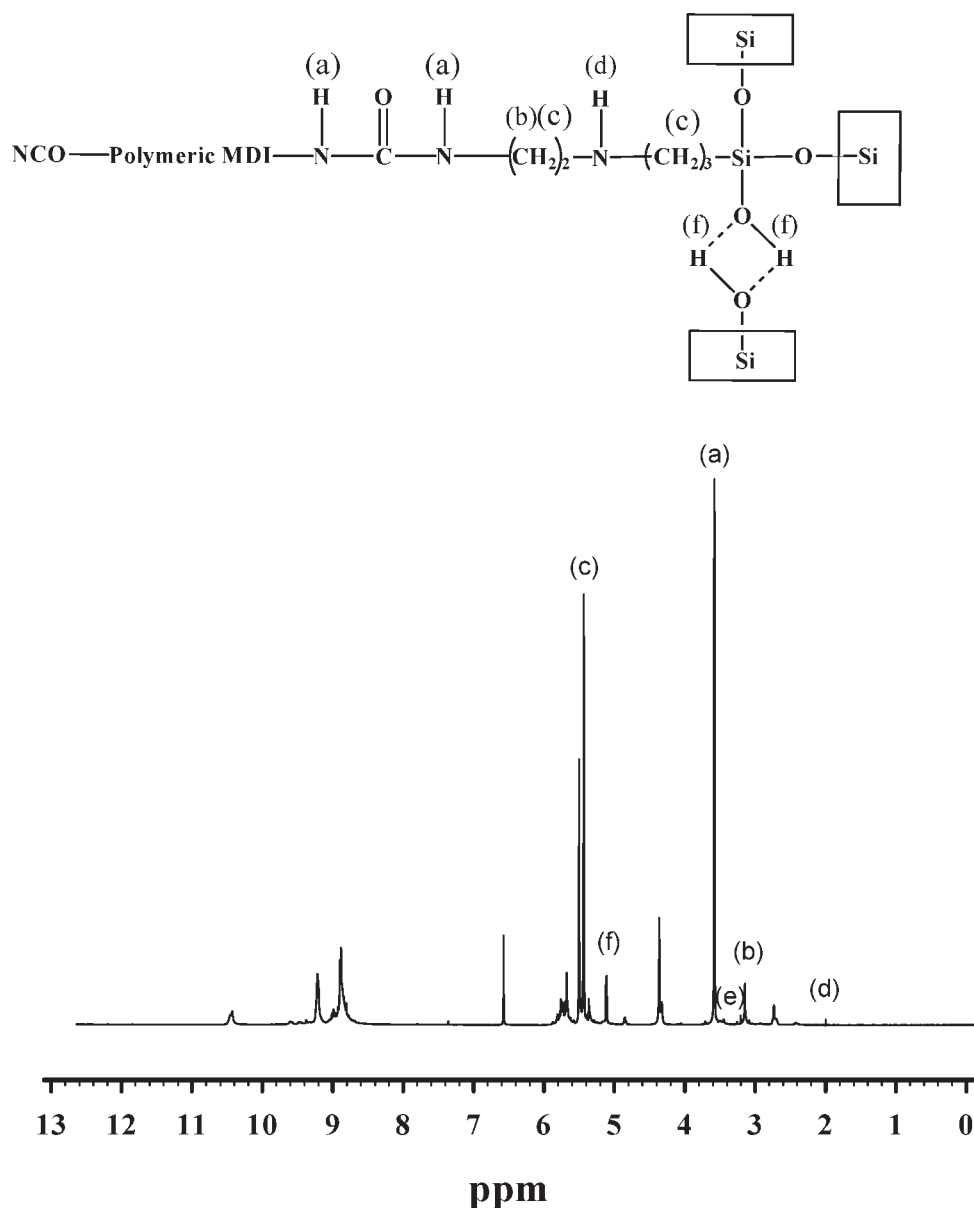
Figure 3 <sup>1</sup>H-NMR spectrum of the PMDI/silane coupling agent mixture.

nanocomposite foam samples were measured under ambient conditions with an Instron (Canton, OH) model 4467 Universal Testing Machine. A flexural test was performed according to KS M3830. The size of the specimen was  $25 \times 120 \times 20 \text{ mm}^3$  (width  $\times$  length  $\times$  thickness). The span distance was 100 mm, and the speed of the crosshead movement was 10.00 mm/min. A compressive test was performed according to ASTM D 1621. The size of the specimen was  $30 \times 30 \times 30 \text{ mm}^3$  (width  $\times$  length  $\times$  thickness), and the speed of the crosshead movement was 3.00 mm/min. The strengths of 10 specimens per sample were measured and averaged for each mechanical test.

## RESULTS AND DISCUSSION

Figure 1(a–d) shows the FTIR spectra of the silane coupling agent, organoclay, PMDI/silane coupling

agent mixture, and PMDI/silane coupling agent/organoclay mixture, respectively. The band at about  $1075 \text{ cm}^{-1}$  is assigned to the Si–O–C stretching vibration of Si–OCH<sub>3</sub> of the coupling agent in Figure 1(a). A broad absorbance between 1000 and 1050  $\text{cm}^{-1}$  is attributed to the stretching vibration of Si–OH in the organoclay in Figure 1(b). In the spectrum of the PMDI/silane coupling agent mixture, a band at  $1075 \text{ cm}^{-1}$  is due to the Si–O–C stretching vibration of Si–OCH<sub>3</sub> of the coupling agent, and the band at  $1650 \text{ cm}^{-1}$  is due to the urea group formed as a result of the addition reaction between –NCO in PMDI and –NH<sub>2</sub> in the coupling agent in Figure 1(c). Also, the Si–O–Si covalent bond was newly formed by the coupling reaction of the silane coupling agent (Si–OCH<sub>3</sub>) and organoclay surface (Si–OH) in the PMDI/silane coupling agent/organoclay mixture, and the characteristic



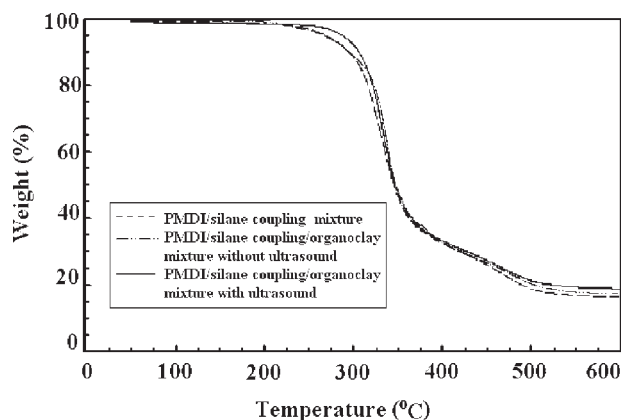
**Figure 4** <sup>1</sup>H-NMR spectrum of the PMDI/silane coupling agent/organoclay mixture.

stretching vibration of Si—O—Si appears at about 1000–1110 cm<sup>-1</sup> in Figure 1(d).

FTIR spectra from our experiments confirm the well-known fact that as the length of the siloxane chain increases, the band broadens and splits.<sup>33</sup> Refining of the modified organoclay was conducted with DMF as a solvent, and then unreacted PMDI in the PMDI/silane coupling agent/organoclay mixture was washed off before the spectroscopic characterization to make sure that all composites were covalently bonded. Characteristic spectral peaks of the PMDI/silane coupling agent/organoclay compound were observed at about 3305 (hydrogen-bonded —NH stretching vibration), 2275 (asymmetric —NCO stretching), and 1650–1730 cm<sup>-1</sup> (—C=O stretching vibration), and Si—O—Si was observed at

1000–1100 cm<sup>-1</sup> (Si—O—Si stretching vibration). The compound would be a precursor to react with polyols to form PU chains.

The proposed schematic diagrams for the exfoliation process of organoclay layers of the PMDI/silane coupling agent/organoclay mixture are shown in Figure 2. Figure 2(a–d) shows the structures of the PMDI/silane coupling agent mixture, organoclay, organoclay, and PMDI/silane coupling agent mixture and the exfoliation of the organoclay layers with the PMDI/silane coupling agent/organoclay mixture. The results of FTIR shown in Figure 1(c) are schematized in Figure 2(a), which shows the urea linkage between the —NCO group of PMDI and —NH<sub>2</sub> group of the silane coupling agent.



**Figure 5** TGA thermograms of (a) the PMDI/silane coupling agent mixture, (b) the PMDI/silane coupling agent/organoclay mixture without ultrasound, and (c) the PMDI/silane coupling agent/organoclay mixture with ultrasound.

Figures 3 and 4 show  $^1\text{H-NMR}$  spectra of the PMDI/silane coupling agent and PMDI/silane coupling agent/organoclay mixture, respectively. The PMDI/silane coupling agent mixture was prepared by the reaction between the isocyanate ( $-\text{NCO}$ ) group of PMDI and the amino ( $-\text{NH}_2$ ) group of the silane coupling agent, and this reaction is confirmed by the  $^1\text{H-NMR}$  spectrum shown in Figure 3. The  $^1\text{H-NMR}$  spectrum of the PMDI/silane coupling agent/organoclay mixture is shown in Figure 4. The mixture was prepared by the coupling reaction of the trimethoxysilyl ( $-\text{SiOCH}_3$ ) group terminated PMDI and hydroxyl group on the organoclay. The signal at  $\delta = 3.7$  ppm (a) is attributed to the protons of the urea bond ( $-\text{NHCONH}-$ ), and the signals at  $\delta = 3.2$  ppm (b) and  $\delta = 5.2$  ppm (c) are ascribed to the protons of ethyl ( $-\text{N}-\text{CH}_2\text{CH}_2-\text{N}-$ ) and ethyl ( $-\text{CH}_2\text{CH}_2-$ ), respectively. The proton of  $-\text{C}-\text{NH}-\text{C}-$  can be observed at  $\delta = 2.0$  ppm (d). The proton signal of trimethoxyl ( $-\text{OCH}_3$ ) in the silane coupling agent can be observed at  $\delta = 3.4$  ppm (e), which is not found in Figure 4. The reason that the  $-\text{OCH}_3$  peak ( $\delta = 3.4$ ) disappeared for the PMDI/silane coupling agent/organoclay mixture in Figure 4 is believed to be the fact that the bonding of  $\text{Si}-\text{O}-\text{Si}$  is formed by the coupling reaction of  $\text{Si}-\text{OH}$  at the organoclay surface and  $-\text{Si}-\text{OCH}_3$  of the coupling agent.

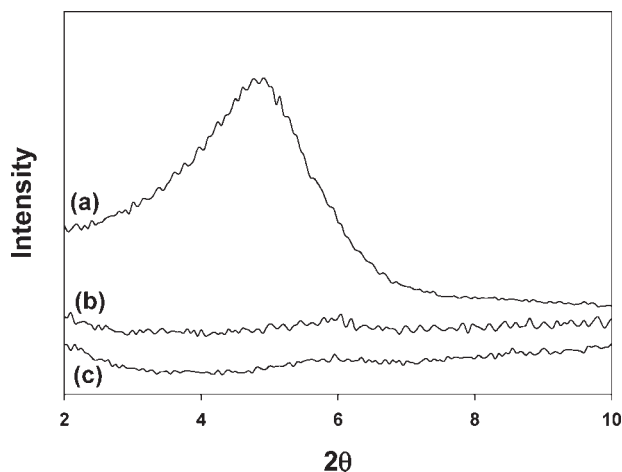
As shown in Figure 5, the thermal degradation of the PMDI/silane coupling agent mixture and PMDI/silane coupling agent/organoclay mixture with and without ultrasound was investigated by TGA under a nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . The PMDI/silane coupling agent/organoclay mixture with ultrasound degrades at a higher temperature than the PMDI/silane coupling agent mixture. During thermal degradation, the effect of

the organoclay in the organic compound can be explained by a decrease in the diffusion of oxygen and volatile products throughout the composite. In addition, the exfoliated and dispersed organoclay layers make the pathway of the diffusing gas more extended.

The organoclay with the silane coupling agent achieved the effective breakup of the organoclay agglomerates and exfoliation of the silicate layers in polymer chains. Also, the crosslinked structure and covalent bond with high energy from the reaction of  $-\text{SiOCH}_3$  and  $-\text{SiOH}$  on the surface of organoclay were the reasons for the increase of the degradation temperature of the PMDI/silane coupling agent/organoclay. Therefore, we suggest that the increase of the degradation temperature of the PMDI/silane coupling agent/organoclay may be due to the intercalation of the organoclay by the chemical reaction between the organoclay surface and coupling agent attached to PMDI.

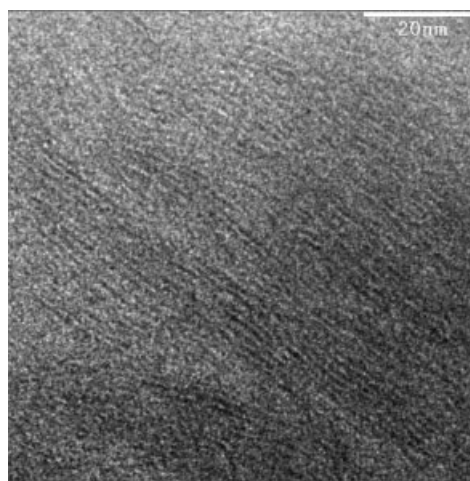
Figure 6 shows the X-ray diffraction (XRD) patterns of the organoclay, PU/organoclay nanocomposite, and PU/silane coupling agent/organoclay nanocomposite. The (001) peak of the organoclay layers can be observed at  $2\theta = 4.75^\circ$  ( $18.5 \text{ \AA}$ ), as shown in Figure 6(a). For the PU/organoclay nanocomposites both with and without the silane coupling agent, XRD patterns give no information about the structural regularity in Figure 6(b,c). Because there is no peak, it is suggested that the organoclay is uniformly dispersed in the polymer matrix. The difference in the degrees of dispersion of the organoclay among the composites shown in Figure 6 was investigated with TEM, and the data are shown in Figure 7.

Figure 7(a-c) shows the TEM morphology of the organoclay, PU/organoclay nanocomposite, and

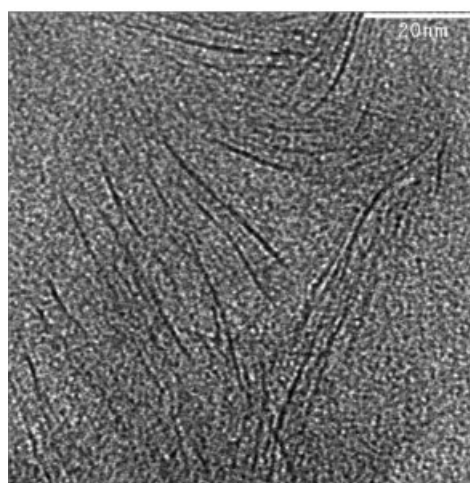


**Figure 6** XRD patterns of (a) the organoclay, (b) the PU/organoclay nanocomposite, and (c) the PU/silane coupling agent/organoclay nanocomposite.

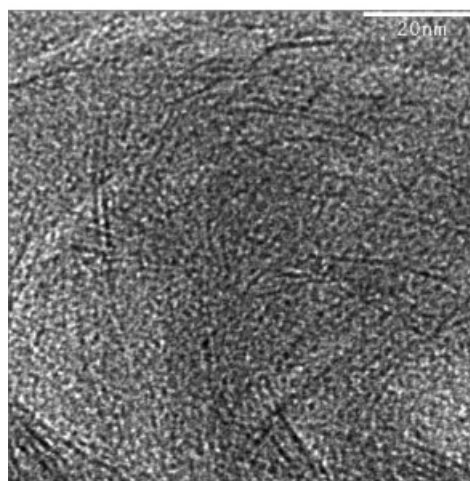




(a)

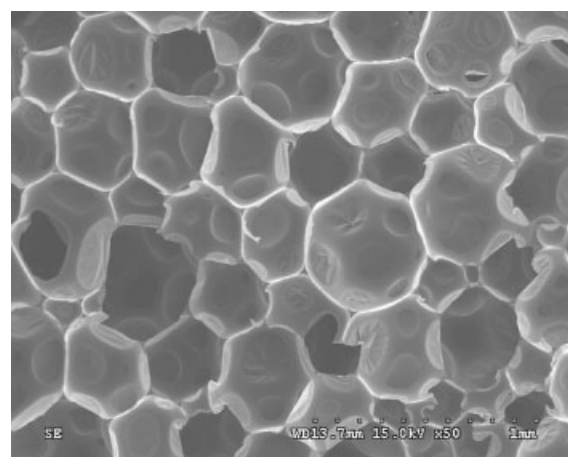


(b)

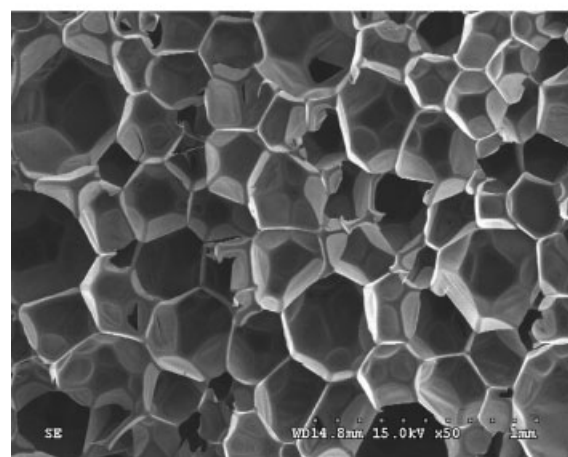


(c)

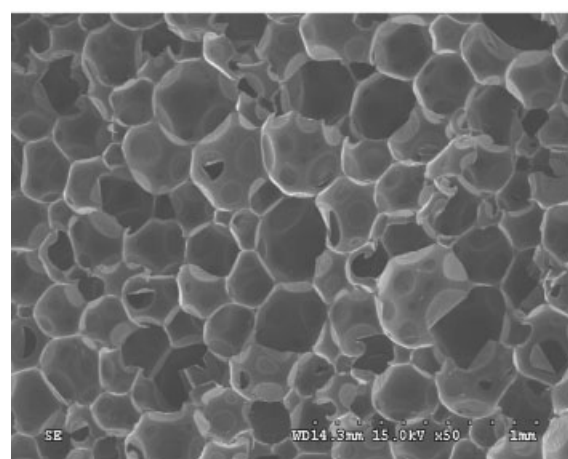
**Figure 7** TEM images of (a) the organoclay, (b) the PU/organoclay nanocomposite, and (c) the PU/silane coupling agent/organoclay nanocomposite.



(a)



(b)



(c)

**Figure 8** SEM images of (a) the PU/organoclay nanocomposite foam, (b) the PU/silane coupling agent/organoclay nanocomposite foam without ultrasound, and (c) the PU/silane coupling agent/organoclay nanocomposite foam with ultrasound.

**TABLE II**  
**Mechanical Strength and Thermal Conductivity of PU/Silane Coupling Agent/**  
**Organoclay Nanocomposite Foams**

Property	PU/organoclay foam	PU/silane coupling agent/organoclay foam	
		Without ultrasound	With ultrasound
Compressive strength (MPa)	1.512	1.522	1.523
Flexural strength (MPa)	1.980	2.041	2.256
Thermal conductivity (W/m h °C)	0.0250	0.0234	0.0230

PU/silane coupling agent/organoclay nanocomposite. The organoclay layers have completely stratiform structures, as shown in Figure 7(a). PU/organoclay nanocomposites without the coupling agent show partially exfoliated structures with some part of the intercalated organoclay layers in Figure 7(b). However, as shown in Figure 7(c), the organoclay layers are delaminated and disordered in the PU/organoclay nanocomposite with the silane coupling agent. The exfoliation step can be described as follows: the two outermost layers in a stack will be pulled apart first, and then the next two outermost layers will be pulled apart.<sup>15</sup> The results of TEM shown in Figure 7 are consistent with the results obtained from the XRD patterns: the *d*-spacing is increased by the penetration of PU into the organoclay layer in the PU/silane coupling agent/organoclay nanocomposites.

Figure 8(a–c) shows the SEM morphology of the PU/organoclay nanocomposite foam, PU/silane coupling agent/organoclay nanocomposite foam without ultrasound, and PU/silane coupling agent/organoclay nanocomposite foam with ultrasound. The effects of PMDI with the silane coupling agent on the cell morphology of the PU/silane coupling agent/organoclay nanocomposite foams are shown in Figure 8. PMDI with the silane coupling reaction increases the dispersibility of the organoclay in the PU/silane coupling agent/organoclay nanocomposite foam in comparison with the PU/organoclay nanocomposite foam. In Figure 8(a–c), the cell size of the PU/organoclay foam and PU/silane coupling agent/organoclay nanocomposite foams are shown to be 320, 280, and 250  $\mu\text{m}$ , respectively. Therefore, it is suggested that the smaller cell size (by 70  $\mu\text{m}$ ) of the PU/silane coupling agent/organoclay nanocomposite foam with ultrasound in comparison with the PU/organoclay foam is perhaps due to the enhanced exfoliation structure of the organoclay. The exfoliated organoclay layers with the silane coupling reaction in the PU matrix can act as nucleation agents and serve as sites for bubble growth, with the formation of new bubbles not being necessary.<sup>12–14</sup> Therefore, we suggest that the reduction in the cell size of the PU/silane coupling agent/organoclay

nanocomposite foams may be due to the nucleation effect of the exfoliated organoclay.

Table II shows the mechanical properties and thermal conductivity of the PU/organoclay foam and PU/silane coupling agent/organoclay nanocomposite foams with and without ultrasound. Table II shows that the compressive and flexural strengths of the PU/silane coupling agent/organoclay nanocomposite foam without ultrasound are somewhat higher than those of the PU/organoclay nanocomposite foam. For the PU/silane coupling agent/organoclay nanocomposite foam with ultrasound, the compressive and flexural strength can be observed to increase slightly in comparison with those of the PU/silane coupling agent/organoclay nanocomposite foam without ultrasound. Therefore, it is suggested that the silane coupling agent acts to enhance the exfoliation of the organoclay layers in the PU matrix.

Also, Table II shows the thermal conductivity of the PU/organoclay foam and PU/silane coupling agent/organoclay nanocomposite foams with and without ultrasound. As shown in Table II, the thermal conductivity of the PU/silane coupling agent/organoclay nanocomposite foam without ultrasound is 0.0234 W/m h °C and decreases appreciably in comparison with that of the PU/organoclay nanocomposite foam (0.0250 W/m h °C). For the PU/silane coupling agent/organoclay nanocomposite foam with ultrasound, the thermal conductivity is 0.0230 W/m h °C, and it decreases slightly in comparison with that of the PU/silane coupling agent/organoclay nanocomposite foam without ultrasound (0.0234 W/m h °C). The results of Table II suggest that the silane coupling agent affects the mechanical properties and thermal conductivity of PUF more than ultrasound does.

## CONCLUSIONS

The characteristics of PU/silane coupling agent/organoclay nanocomposite foams, which were chemically bonded by the silane coupling reaction between the polymer chain and clay, were investigated. Analytical data from FTIR and <sup>1</sup>H-NMR revealed that a

new urea functional group was formed through the reaction of NCO of PMDI and  $\text{NH}_2$  of the silane coupling agent. The Si—O—Si functional group was also newly formed by the reaction of OH at the clay surface and  $\text{OCH}_3$  of the coupling agent.

XRD profiles and TEM micrographs showed that the interlayer distance of the organoclay in the PMDI/silane coupling agent/organoclay composite increased, and the organoclay in the composite appeared to be exfoliated and uniformly dispersed. The cell size of the PU/organoclay nanocomposite foam produced with the silane coupling agent was smaller and more uniform than that of the nanocomposite produced without the silane coupling agent. The thermal conductivity of the nanocomposite with the silane coupling agent was also lower, and this resulted in improved insulation properties.

It can be concluded that the smaller cell size and lower thermal conductivity of the PU/organoclay nanocomposite foams were mainly due to the enhanced exfoliation of the clay layers by the silane coupling reaction between the organoclay surfaces and the polymer chains.

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